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THEORETICAL CONSIDERATIONS GOVERNING CONCENTRATIONS IN FUMIGATION[1]

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Fumigation is generally accomplished by introducing a volatile liquid or a gas into an enclosure containing the materials to be fumigated. Its effectiveness depends on the exposure time and the concentration at a given temperature. Since fumigation chambers are not usually designed to hold pressures above atmospheric, the vaporizing liquid or the compressed gas that is introduced displaces an equivalent volume of air-fumigant mixture. Losses of fumigant due to other factors such as leakage or wall absorption also occur, and if these are known, the concentration of the fumigant at any time can be calculated.

This discussion applies only to chambers operating under atmospheric conditions, which contain only air initially and remain at atmospheric pressure throughout the fumigation period. Vacuum fumigation will not be considered.

The concentration of the fumigant in the chamber at any time is a function of two factors--the quantity introduced per unit volume of chamber space, and the rate of leakage through the walls and crevices of the chamber, both as displacement loss during input and by diffusion to the outside atmosphere during the fumigation period. As a basis for calculation it is assumed that the following conditions are maintained: (1) the rate of input of the fumigant is constant, (2) the input time is much shorter than the entire fumigation period, (3) the fumigation mixture in the chamber is in the gas phase and homogeneous at all times, (4) the components of the mixture are always in the same proportion (except as will be mentioned later), (5) the walls of the chamber are rigid and allow slight interchange between the gases in the chamber and the outside atmosphere, and (6) the leakage rate of gas (fumigant plus air) to the outside atmosphere is constant.

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As fumigant is discharged into the chamber, it vaporizes and mixes with the air in the chamber, displacing an equal volume of air to the outside atmosphere. The gas displaced initially consists only of air, but it gradually becomes richer in fumigant, until the concentration of incoming fumigant is in equilibrium with that of the gas being displaced. The concentration upon completion of input will thus be a function of the volume and rate of fumigant input and the quantity lost by displacement.

After the input of fumigant is completed, there is no longer any displacement loss. Since the fumigation period is much longer than the input time, leakage loss is usually the more important factor at this period. Rate of leakage of fumigant is highest at the time of its maximum concentration, and then gradually diminishes. Since the chamber gases are in continuous motion as a result of fan circulation, the leakage rates of different gases are more or less the same. However, when differences in leakage rates of the components of the fumigant are observed, the gas whose leakage rate appears to be abnormally high may be adsorbed on the interior surfaces or removed in some other manner, such as chemical reaction with materials in the chamber, decomposition, or condensation.

Equations[4/]

Based on these considerations and by means of the calculus, equations have been developed to express the concentration relationships. The symbol notations and mathematical derivations of these equations will be found in the appendix of this report. The equations are similar to those of monomolecular or monoatomic reactions, such as radioactive decay, in which the reaction rate (leakage) is proportional to the concentration of reactant (fumigant) at any moment during the reaction (fumigation).

<u>During Fumigant Input</u>

$$S_1 = (100/Z)(1 - e^{-Z\theta}) + S_o e^{-Z\theta} \qquad (1)$$

$$\theta = (2.303/Z) \log [(100 - ZS_o)/(100 - ZS_1)] \qquad (2)$$

Usually $S_o = 0$, and the equations become

$$S_1 = (100/Z)(1 - e^{-Z\theta}) \qquad (1')$$

$$\theta = (2.303/Z) \log [100/(100 - ZS_1)] \qquad (2')$$

<u>Fumigation Period</u>

$$\log S = \log S_1 - 0.4343\ kt'/V \qquad (3)$$

4/ The ten text equations (1, 2, 1', 2', 3, 4, 5, 6, 7, and 8) are derived in the appendix, where they are designated A-14, A-13, A-14', A-13', A-17, A-34, A-31, A-22, A-24, and A-26, respectively.

Interpretation and Utilization of Equations

Quantity of Fumigant Dispensed and Initial Concentration. From equations 1 and 2 the quantity of fumigant dispensed, Q, and the initial concentration, S_1, can be calculated from each other. The volume of fumigant gas input can be estimated from the weight of fumigant discharged and the ideal gas law. Input rate, I, can be determined by timing the input. In experiments at our laboratory the fumigant was dispensed from pressure cylinders, and the cylinder was weighed before and after discharge and the time of input noted in order to calculate I. The leakage rate, k, must be determined separately for the chamber in question; it is best done in advance by chemical analysis. It was found convenient to discharge dichlorodifluoromethane into the chamber and to determine it by means of thermal-conductivity measurements (1) at frequent intervals. Methyl bromide (4) and similar gases could also have been used. k can be calculated from the slope of a plot of log S against t'. If k is small and the input time is short, k may be neglected (Z = 1) for approximating Q and S_1 from each other.

Maximum Obtainable Concentration ($S_0 = 0$). From equation 1' we note that the maximum possible concentration is less than 100/Z.

Input Rate. From equation 1 we can estimate that, for a given fumigation dosage, the faster the input rate, I, the lower will be Z, and consequently the greater will be the concentration at the completion of the input. Thus, to increase initial fumigant concentration, the input rate should be as fast as possible.

Maintenance of a Constant Fumigant Concentration. It may be necessary or desirable to maintain a fumigant concentration at a constant value after the input is completed. This may be accomplished by means of a continuous secondary input, I_2, of fumigant into the chamber to balance the loss due to leakage. The rate of the secondary input is:

$$I_2 = k\, S_1/(100 - S_1) \qquad (4)$$

Half-life of Fumigant Concentration. The time required for the concentration of fumigant to fall to half its original value may be calculated as follows:

$$t'_{1/2} = 0.693\ V/k \qquad (5)$$

Plotting of Concentration-Time Curves. It is useful to plot log S against t, since from equation 3 we can see that the relationship will be linear. The slope of this line, m_1, is equal to - 0.4343 k/V, and we can therefore calculate k from m_1.

$$k = 2.303\ Vm_1$$

Additional Meanings of k. We have defined k as the rate of leakage, and have assumed that the fumigant is inert and is not removed from the chamber in any other way. In certain cases, however, this may not be so, and k includes all avenues of loss of fumigant. We may then redefine k as the sum of all these loss rates.

$$k = \sum k_i$$

where k_i = any individual loss rate, such as that due to leakage, absorption, condensation, or chemical reaction.

Determination of Exposure. Exposure (frequently referred to as Ct) is usually measured by plotting concentration against time over the fumigation period and then estimating the area under the curve. This may also be done by calculations based on the equations that have been derived. It is convenient to split up exposure, E, into two parts, E_I during input and E_{II} the fumigation period. We shall consider only the usual case where the fumigation is started at zero concentration of fumigant. Since it is customary to express E as a function of weight concentration of the active ingredient per unit volume (milligrams/liter) and time (hours), a constant, A, and the factor 1/60 are introduced to effect these conversions, respectively, from percent concentration and time in minutes.

$$E_I = AV\,(100\,\theta - S_1)/60\,(I + k) \qquad (6)$$

$$E_{II} = AVS_1N/60\,k \qquad (7)$$

where $N = 1 - e^{-kt'/V}$

$$e^{kt'/V} = \log^{-1}(0.4343\,kt'/V)$$

and $E = E_I + E_{II}$

From these equations we may also calculate the necessary input, Q, for any desired E at a given time period, t'. Usually E_I is smaller than E_{II} and may be neglected for approximation purposes.

$$\therefore E = E_{II}$$

$$\theta = (2.303/Z)\log\left[1.67\,ANV/(1.67\,ANV - kZ\,E_{II})\right] \qquad (8)$$

Calculation of E from Analytical Data. If we can neglect E_I, we merely have to calculate E_{II}, as follows: Plot log S against time, and determine k from the slope, m. Extrapolate the curve back to t' = 0 (at time of completion of input) and estimate log S_1 and hence S_1. Knowing V, t', and A, we can calculate E_{II} from equation 7.

Maximum Obtainable E. From equation 8 we can estimate the maximum obtainable E to be 1.67 ANV/kZ.

Application of Equations to Experiment

In the course of fumigation work in cooperation with the Army Chemical Corps, in tests of the efficiency of ethylene oxide as a sterilizing agent, data were collected which may be used in applying the equations just derived. The data are from two fumigation experiments at 90° F. with 60 pounds of 10 percent ethylene oxide plus 90 percent carbon dioxide in the first, and 50 pounds of 12 percent ethylene oxide plus 88 percent dichlorodifluoromethane in the other.

The carbon dioxide and dichlorodifluoromethane acted as propellants to dispense the ethylene oxide, and also as flame suppressants to prevent a fire hazard (3). From time to time samples from the gas mixture in an approximately 977-cubic-foot airplane fuselage used as a fumigation chamber were analyzed chemically (1). Results are shown in table 1. Plots of the log of concentration against fumigation time are shown in figure 1.

Table 1.--Concentrations (volume percent) of ethylene oxide and propellant in 977 cubic-foot airplane fuselage. Temperature 90° F.

Time (minutes)	Ethylene oxide	Propellant	Total fumigant	Ratio propellant to ethylene oxide
Ethylene oxide + carbon dioxide at input rate of 3,874 liters/minute				
0 1/	4.2	37.6	41.8	9.0
0 2/	3.6	35.1	38.7	9.8
7	3.5	34.3	37.8	9.8
35	3.0	31.3	34.3	10.4
65	2.4	27.5	29.9	11.4
152	1.6	19.7	21.3	12.3
k	149	96	--	--
$t_{1/2}$ (min.)	128	182	--	--
Ethylene oxide + dichlorodifluoromethane at input rate of 568 liters/minute				
0 1/	4.9	13.2	18.1	2.671
0 2/	4.6	14.3	18.9	3.1
15	4.4	14.1	18.5	3.2
45	3.8	9.9	13.7	2.6
75	3.0	10.1	13.1	3.4
165	2.3	7.2	9.5	3.1
k	118	110	--	--
$t_{1/2}$ (min.)	162	169	--	--

1/ Calculated from theoretical equations.

2/ By extrapolation of analytical data.

Figure 1.--Plots of the logs of concentrations of ethylene oxide and propellant against fumigation time.

From the data certain observations may be made:

Although equal weights of ethylene oxide (6 pounds) were used in each fumigation in the same airplane fuselage, the mixture containing dichlorodifluoromethane resulted in a higher concentration of ethylene oxide. This is in accordance with equation 1, and is due to the greater volume of total fumigant discharged into the airplane by the carbon dioxide mixture. At higher concentrations this difference would increase greatly. Greater quantities of the ethylene oxide-carbon dioxide mixture than of the ethylene oxide-dichlorodifluoromethane mixture will be needed to reach a given concentration of ethylene oxide, and the latter mixture will also be able to reach a greater máximum concentration in a given chamber no matter how much fumigant is dispensed. The initial concentrations calculated from the theoretical equations (based on an estimated k value of 100) are in good agreement with the results found.

The plots of log concentration against time are linear, as predicted by equation 3.

The k values for both propellants were of the same order of magnitude, suggesting that their loss mechanism was of the same type. The k values for ethylene oxide were higher, however, especially in the first experiment, perhaps because of loss by absorption on the walls and other internal surfaces of the chamber.

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Appendix

Notation	Unit	Meaning
Q	liters	Volume of input gas
V	do.	Volume of fumigation chamber
X	do.	Volume of fumigant gas in chamber
L	do.	Volume of outgoing gas due to leakage
I	liters/minute	Input rate of fumigant
k	do.	Gas-loss rate, $k = -2.303\ Vm$
t	minutes	Time (0 at start of input)
t'	do.	Time of fumigation after input
$t'_{1/2}$	do.	Half-life ($S = S_{1/2}$)
S	percent by volume	Concentration of fumigant
S_o	do.	S at beginning of input
S_1	do.	S at end of input
θ	--	$\theta = Q/V$
Z	--	$Z = (I + k)/I$
E	mg.-hours/liter	Exposure measure, or $Ct = S \times t \times A/60$
C	mg./liter	Concentration of active ingredient ($C = SA$)
A	do.	Conversion factor from percent by volume, $A = C/S$
m	log (% by vol.)/minute	Slope $m = 0.4343\ k/V$
N	--	$N = (e^{kt'/V} - 1)/e^{-kt'/V}$
$e^{kt'/V}$	--	$e^{kt'/V} = \log^{-1} (0.4343\ kt'/V)$

Derivation of Equations

<u>During Input</u>. Change of volume of fumigant gas with time in the fumigation chamber:

$$\frac{dx}{dt} = \frac{dQ}{dt} - \frac{x}{V}.\frac{dQ}{dt} - \frac{k}{V}.\frac{dL}{dt} \qquad \text{(A-1)}$$

where $\frac{dQ}{dt}$ = input, $\frac{x}{V}.\frac{dQ}{dt}$ = displacement, and $\frac{k}{V}.\frac{dL}{dt}$ = leakage

But $I = \frac{dQ}{dt}$ (A-2)

and $K = \frac{dL}{dt}$ (A-3)

Substituting for $\frac{dQ}{dt}$ and $\frac{dL}{dt}$ in equation A-1

$$\frac{dx}{dt} = I - xI/V - xk/V \qquad \text{(A-4)}$$

Also $S = 100x/V$ (by definition) (A-5)

Differentiating s with respect to x

$$dx = (V/100)\ ds \qquad \text{(A-6)}$$

Substituting for x and dx in equation A-4

$$\frac{ds}{dt} = 100\ I/V - S\ (I + k)/V \qquad \text{(A-7)}$$

and rearranging and setting up for integration

$$\int_0^{s_1} ds/[100\ I - (I + k)\ S] = \int_0^{t_1} (1/V)\ dt \qquad \text{(A-8)}$$

Integrating between limits

$$t_1 = [V/(I + k)]\ \ln \left[\frac{100\ I - (I + k)\ S_0}{100\ I - (I + k)\ S_1}\right] \qquad \text{(A-9)}$$

But $Q = \int_0^{t_1} I\ dt = It_1$ (A-10)

$$t_1 = Q/I \qquad \text{(A-11)}$$

Substituting for t_1 in equation A-9 and converting to common logarithms,

$$Q/I = [V/(I + k)] \ln \left[\frac{100\ I - (I + k)\ S_o}{100\ I - (I + k)\ S_1}\right] \qquad \text{(A-12)}$$

But $\theta = Z/V$ and $Z = (I + k)/I$

Substituting these values in equation A-12

$$\theta = (1/Z) \ln [(100 - Z\ S_o)/(100 - Z\ S_1)] \qquad \text{(A-13)}$$

and solving for S_1

$$S_1 = (100/Z)(1 - e^{-Z\theta}) + S_o e^{-Z\theta} \qquad \text{(A-14)}$$

If $S_o = 0$, equations A-13 and A-14 become

$$\theta = (1/Z) \ln [100/(100 - ZS_1)] \qquad \text{(A-13')}$$

and $S_1 = (100/Z)(1 - e^{-Z\theta})$ (A-14')

<u>Fumigation Period</u>: Since the input is completed,

$I = 0$, and equation A-7 becomes

$$\frac{dS}{dt} = Sk/V \qquad \text{(A-15)}$$

Rearranging and setting up for integration between limits

$$\int_{S_1}^{S} (1/S)\ ds = -(k/V) \int_{o}^{t'} dt \qquad \text{(A-16)}$$

Integrating equation A-16

$$\log S = \log S_1 - 0.4343\ kt'/V \qquad \text{(A-17)}$$

since $k = 2.303\ Vm$, equation A-17 becomes

$$\log S = \log S_1 + mt' \qquad \text{(A-17')}$$

or $S = S_1 e^{2.303\ mt'}$ (A-17'')

<u>Determination of E During Input</u>. By definition E_I = area under curve of concentration vs. time

$$\therefore\ E_I = \int_{o}^{t'} (C/60)\ dt \qquad \text{(A-18)}$$

But C = AS, and substituting for C in equation A-18

$$E_I = (A/60)\int_0^t S dt \qquad \text{(A-19)}$$

From equation A-11

$$t = Q/I = \theta V/I \qquad \text{(A-11)}$$

Differentiating equation A-11 with respect to I,

$$dt = (V/I)\, d\theta \qquad \text{(A-20)}$$

Substituting for S from equation A-14, and t and dt from equations A-11 and A-20 in equation A-19,

$$E_I = (AV/60I)\int_0^\theta [S_o e^{-\theta Z} + 100\,(e^{\theta Z} - 1)/Ze^{\theta Z}]\, d\theta \qquad \text{(A-21)}$$

After rearranging equation A-21, and integrating between limits (assuming $S_o = 0$)

$$E_I = AV\,(100\,0 - S_1)/60\,(I + k) \qquad \text{(A-22)}$$

<u>Determination of E During Fumigation Period.</u> Equation A-17'' may be converted to

$$S = S_1\, e^{-kt'/V} \qquad \text{(A-17''')}$$

Substituting C = SA for C in equation A-18,

$$E_{II} = (A/60)\int_0^{t'} S_1 e^{-kt'/V}\, dt \qquad \text{(A-23)}$$

Integrating between limits and substituting N,

$$E_{II} = AVS_1\, N/60k \qquad \text{(A-24)}$$

Also $E = E_I + E_{II}$

Substituting the value for S_1 from equation A-14' in equation A-24, and solving for θ,

$$\theta = (2.303/Z)\log [1.67\, ANV/1.67\, ANV - kZE_{II}] \qquad \text{(A-26)}$$

Under most conditions the input time is short and E_I can be neglected.

$$E = E_{II}$$

Maximum Obtainable E for a Given t'. In order for equation A-26 to have meaning, the quantity 1.67 ANV - kZ E_{II} must be greater than zero. The limit value of E_{II} can be calculated by equating

$$1.67\ ANV > kZ\ E_{II}\ max$$

$$\therefore\ E_{II}\ max < (1.67\ ANV/kZ) \qquad \text{(A-27)}$$

Maximum Obtainable Fumigant Concentration (S max). If we assume $S_o = 0$, we may apply the reasoning just used for equation A-26 to equation A-13', and $100 > Z\ S_1$

$$\therefore\ S_1\ max < (100/Z) \qquad \text{(A-28)}$$

Half-life ($t'_{1/2}$).

By definition $S = S_{1/2}$

Substituting in equation A-17',

$$\log (S_{1/2}) = \log S_1 + m\ t'_{1/2} \qquad \text{(A-29)}$$

On rearranging, this becomes

$$t'_{1/2} = \frac{\log (1/2)}{m} \qquad \text{(A-30)}$$

$$\therefore\ t'_{1/2} = -\ 0.30103/m = 0.693\ V/k \qquad \text{(A-31)}$$

Continuous Secondary Input to Compensate for Leakage. To accomplish this, equation A-7 becomes

$$\frac{ds}{dt} = 0 = (100\ I_2/V) - [S_1\ (I_2 + k)/V] \qquad \text{(A-32)}$$

Rearranging,

$$100\ I_2/V = (I_2 + k)\ S_1/V \qquad \text{(A-33)}$$

$$\therefore\ I_2 = k\ S_1/(100 - S_1) \qquad \text{(A-34)}$$